Nanoscale surface relaxation of a membrane stack

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Recent measurements of the short-wavelength ($\sim$ 1–100 nm) fluctuations in stacks of lipid membranes have revealed two distinct relaxations: a fast one (decay rate of ~ 0.1 ns^{-1}), which fits the known baroclinic mode of bulk lamellar phases, and a slower one ($\sim$ 1–10 μs^{-1}) of unknown origin. We show that the latter is accounted for by an overdamped capillary mode, depending on the surface tension of the stack and its anisotropic viscosity. We thereby demonstrate how the dynamic surface tension of membrane stacks could be extracted from such measurements.

Self-assembled stacks of membranes are encountered in various industrial and biological systems. They consist of parallel bilayers of amphiphilic molecules separated by microscopic layers of solvent — a structure with the symmetry of a smectic A liquid crystal [1]. Such stacks form lyotropic lamellar phases [2], on which many cleaning and cosmetic products are based. Lamellar bodies are found also in the lung [3] and as multilayer vesicles ("onions") [4]. Membrane stacks made of phospholipids have been widely used to study properties of biological membranes, whereby the large number of identical, equally spaced membranes helps enhance the signal and allows the study of membrane–membrane interactions (e.g., [5]).

The elasticity of membrane stacks is equivalent to that of single-component (thermotropic) smectics [1] and has been extensively studied. The elastic moduli of the stack can be extracted from its equilibrium fluctuations using, e.g., x-ray line shape analysis [6]. By contrast, the hydrodynamics of membrane stacks [7, 8], because of their two micro-phase-separated components, differs from that of thermotropic smectics [9]. An additional hydrodynamic mode appears — the baroclinic (slip) mode — along with a unique dissipation mechanism, in which the membranes and solvent layers develop different average velocities [7]. Experimental studies of hydrodynamic modes in membrane stacks have been rather scarce, the prevalent technique being dynamic light scattering [8], whose spatial resolution is limited by the wavelength of light.

In a recent experiment using neutron spin-echo spectrometry, Rheinstädter, Häußler, and Salditt (RHS) have provided a first look at the relaxation of membrane stacks at short wavelength (1–100 nm) and short time (1–10^3 ns) [10]. Their system consisted of several thousands of dimyristoylphosphatidylcholine (DMPC) phospholipid

bilayers, self-assembled into a stack of $d \sim 5$ nm periodicity. The system was studied at temperatures above and below the lipid melting point, corresponding to fluid and gel-like membranes, respectively. In both cases the measured dynamics consisted of two distinct exponential relaxations. The dispersion relation of the faster relaxation (decay rate of ~ 0.1 ns^{-1}) could be well fitted in the fluid-membrane case to that of the baroclinic mode of a bulk lamellar phase [11], while the slower mode (decay rate of $\sim$ 1–10 μs^{-1}) was left unexplained. We demonstrate below that this slower relaxation is well accounted for by a surface mode, i.e., a perturbation which is localized within a finite penetration depth from the surface of the stack.

In a recent publication [12] we have addressed the surface dynamics of membrane stacks, highlighting the qualitative differences from the surface dynamics of both simple liquids and thermotropic smectics [13]. These differences arise from the slip dissipation mechanism, which is absent in simple liquids and thermotropic smectics but is usually dominant in lyotropic lamellar phases. Although the formulation in Ref. [12] is general, its analysis is focused on a very different domain (larger wavelengths and slower rates) from that sampled by RHS. In that domain the slip dissipation dominates and, consequently, the surface relaxation is governed by an overdamped diffusive mode, whose decay rate Γ increases quadratically with the wavevector q. In this Brief Report we present a slight adaptation of that theory for a large-q, high-Γ regime such as that of RHS.

The general surface dynamics of membrane stacks is quite complex, depending on several restoring and dissipation mechanisms [12]. Three moduli are associated with the restoring forces: the compression modulus B, bending modulus K, and surface tension γ. Viscous dissipation is characterized (in the limit of incompressible flow) by three viscosity coefficients [7], denoted η_{M}, η_{T}, and η_{V}. The coefficient η_{M}, associated with differences in the lateral velocity across layers (sliding viscosity), is much smaller than the other two, which correspond to

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the viscous response to deformations of the lipid membranes. We use the parameter $\Theta = 2(\eta_T + \eta_V)/\eta_M$ to characterize this viscosity anisotropy; it is typically of order 10^2–10^3 [7, 14]. The aforementioned slip motion requires another transport coefficient [7], $\mu \simeq d^2/(12\eta_0)$, where η_0 is the viscosity of the solvent (water) layer.

In view of this richness it is helpful to begin by identifying the dominant contributions to the slower mode of Ref. [10]. First, for the typical parameters of that case — $q \sim 10^{-1}$ nm^{-1}, $\Gamma \sim 1$ μs^{-1}, $\eta_M \sim 10^{-2}$ Pa s, and mass density $\rho \sim 1$ g/cm^3 — one gets a negligible Reynolds number, Re $\sim \rho\Gamma/(\eta_M q^2) \sim 10^{-5}$, implying that inertial modes [13] are irrelevant in the current case. Second, to determine the dominant dissipation mechanism one should compare the friction due to slip, $\mu^{-1}v$ (v being a characteristic relative velocity), with that due to viscous stresses, $\eta_{T,V} q^2 v$, i.e., the dimensionless parameter $S = (\eta_M \mu q^2)^{-1}$ is to be compared with Θ [12]. We find $S \sim 10 \ll \Theta$. Thus, unlike the mode focused on in Ref. [12], in the current large-q case viscous dissipation is dominant. Finally, the relative importance of the three restoring mechanisms depends not only on the surface perturbation wavevector q but also on its penetration depth α^{-1}. Since the value of α is unknown a priori, all three mechanisms should be considered in principle. However, to keep the analysis as simple as possible we shall assume that the surface tension is the dominant factor. This ansatz is motivated by the experimental fact that the rate of RHS's slower mode is linear in $|q|$ at small q (see Fig. 1); the way to get such a linear overdamped dispersion relation is to balance a surface tension stress against a viscous one, $\gamma q^2 u \sim \eta q \Gamma u$ (u being the amplitude of the surface deformation). We will return to the consistency of this assumption later on.

The continuum theory formulated in Ref. [12] is valid for wavelengths much larger than the inter-membrane spacing, $qd \ll 1$. RHS's experiment, however, samples the range $0.1 < qd < 4$. To obtain an extrapolation of the analysis to large q we introduce one last modification to the theory — the distance z from the surface into the stack is discretized, $z \to -dn$ ($n = 0, 1, 2, \ldots$), turning the differential equations of Ref. [12] into finite-difference ones (similar to the analysis of high-q acoustic modes in a crystal). The lateral position x parallel to the membranes is kept continuous, and we consider, for simplicity, a surface perturbation which is uniform in the second lateral direction y.

Within these assumptions Eq. (11) of Ref. [12] yields the following surface mode for the vertical displacements of the membranes, $u_n(x,t)$:

$$\begin{aligned} u_n &= (C_+ e^{-\alpha_+ dn} + C_- e^{-\alpha_- dn})e^{iqx - \Gamma t} \\ \alpha_\pm &= \frac{2}{d}\sinh^{-1}\left(\frac{1}{2}\Theta^{\pm 1/2}|q|d\right). \end{aligned} \quad (1)$$

For sufficiently small q ($qd \ll \Theta^{-1/2}$) the spatial decay coefficients are $\alpha_\pm \simeq \Theta^{\pm 1/2}|q|$, i.e., the mode contains two terms of disparate penetration depths, $\alpha_-^{-1} \gg \alpha_+^{-1}$.

(A qualitatively similar result was obtained for the surface mode analyzed in Ref. [12], yet in the current case the origin of the two differing penetration depths is the large viscosity anisotropy rather than the strong slip dissipation.) In the other limit of $qd \gg \Theta^{1/2}$, as expected, both contributions become localized within a distance of order d from the surface, $\alpha_\pm \simeq (2/d)\ln(\Theta^{\pm 1/2}|q|d)$.

The dispersion relation $\Gamma(q)$ is set by the boundary conditions for the stress tensor at the stack surface, as summarized in Eq. (13) of Ref. [12]. Substituting in that equation the expressions for $\alpha_\pm$ obtained above, we get, within the same approximations,

$$\Gamma(q) = \frac{2\gamma}{\Theta \eta_M d} \times$$
$$\left[\sinh^{-1}\left(\frac{1}{2}\Theta^{1/2}|q|d\right) + \sinh^{-1}\left(\frac{1}{2}\Theta^{-1/2}|q|d\right)\right]. \quad (2)$$

Equation (2) is the main result of our current analysis. For large wavelengths this dispersion relation becomes

$$\Gamma(qd \ll \Theta^{-1/2}) \simeq \frac{\gamma}{2[\eta_M(\eta_T + \eta_V)/2]^{1/2}}|q|. \quad (3)$$

Equation (3) is equivalent to the dispersion relation of an overdamped capillary mode at the surface of a simple liquid having effective viscosity $\eta_{eff} = [\eta_M(\eta_T + \eta_V)/2]^{1/2}$. In the opposite, short-wavelength limit we get

$$\Gamma(qd \gg \Theta^{1/2}) \simeq \frac{\gamma}{(\eta_T + \eta_V)d/2}\ln(|q|d). \quad (4)$$

In this quasi-two-dimensional limit the dependence on the smaller (sliding) viscosity, η_M, disappears, and an effective two-dimensional viscosity emerges, $\eta_{2D} = (\eta_T + \eta_V)d/2$ [15].

Figure 1 shows fits of the dispersion relations for the slower mode, as measured by RHS, to Eq. (2) [16]. (The measurements for $q > 0.5$ nm^{-1} are considered less reliable due to scattering by defects in the stack [10].) The stack periodicity was measured as $d = 5.4$ and 5.6 nm at temperatures $T = 30°$C (fluid membranes) and $19°$C (gel-like membranes), respectively [10]. The value of the sliding viscosity at $30°$C, $\eta_M = 0.016$ Pa s, was independently found from a fit of the faster mode [10]. We are thus left with two fitting parameters in Eq. (2), Θ and γ. For the fluid-membrane case we find $\Theta = 110$ and $\gamma = 5.4$ mN/m. It should be stressed that having two free parameters does not allow for accurate determination of both, and these values should be regarded merely as rough estimates. Nonetheless, the fitted values are of the correct scale. The value for Θ implies $\eta_{T,V} \sim \Theta\eta_M \sim 1$ Pa s, i.e., a viscosity 3 orders of magnitude larger than that of water, which matches the typical effective viscosity of lipid membranes [17]. It also implies an effective two-dimensional viscosity $\eta_{2D} \sim \eta_{T,V}d \sim 10^{-9}$–$10^{-8}$ Pa s m, which agrees well with measurements of the surface viscosity of fluid DMPC membranes [18].

The applicability of the theory to stacks of solid, gel-like membranes should be questioned, as such stacks have
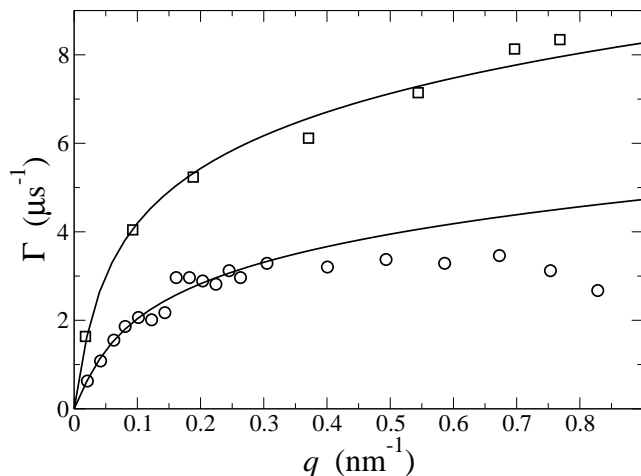
FIG. 1: Dispersion relations for the slower relaxation mode of stacks of DMPC lipid membranes at 30°C (circles) and 19°C (squares). (Data taken from Ref. [10].) The solid lines are fits to Eq. (2) with $d = 5.4$ nm, $\eta_M = 0.016$ Pa s, $\Theta = 110$, and $\gamma = 5.4$ mN/m (lower curve); $d = 5.6$ nm, $\eta_M = 0.016$ Pa s, $\Theta = 350$, and $\gamma = 28$ mN/m (upper curve). The values of d and η_M are taken from Ref. [10]; Θ and γ are fitting parameters.

additional intra-membrane elasticity. The same concern, in fact, should be raised regarding the fluid-membrane case as well, since at the high frequencies considered here the individual membranes are expected to have a viscoelastic response. The fits obtained in Fig. 1 (in particular, the linear behavior for small q) suggest, however, that these additional restoring forces are negligible compared to the surface tension and do not affect the surface relaxation. The fit for $T = 19$°C yields significantly larger values for both the viscosity anisotropy and the surface tension, $\Theta = 350$ and $\gamma = 28$ mN/m, which is the expected trend for stiffer membranes [19]. (In the fit we have assumed that the sliding viscosity η_M does not change much with temperature.)

The elasticity of membrane stacks gives rise to an effective static surface tension, $\gamma_{el} = (KB)^{1/2}$ [1, 20, 21]. The values of K and B in the fluid-membrane state were extracted by RHS from the fit of the faster mode as $K \simeq 1.15 \times 10^{-11}$ N (corresponding to a membrane bending modulus $\kappa = Kd \simeq 14.8\, k_B T$) and $B \simeq 1.08 \times 10^7$ Pa. This yields $\gamma_{el} \simeq 11.1$ mN/m, which is of the same order of magnitude as the high-frequency surface tension fitted above [22].

We now return to check the self-consistency of our assumptions. First, for a mode to be a surface one its penetration depth must be smaller than the total thickness of the sample. The penetration depth found in Eq. (1) is $\alpha_-^{-1} < \Theta^{1/2}/q \lesssim 10^2$ nm, which is at least 1–2 orders of magnitude smaller than the thickness of RHS's films ($\sim 10\ \mu$m). Second, for surface tension to be the dominant restoring force, one should have $\gamma > \gamma_{el}$. This condition can be obtained rigorously [24] but is also realized upon demanding that the stress arising from surface tension, $\gamma q^2 \alpha u$, be larger than both the compression one, $B\alpha^2 u$, and the bending one, $Kq^4 u$. As described above, we actually have $\gamma \sim \gamma_{el}$ and, thus, the assumption can be only marginally fulfilled. Moreover, the omission of the bending terms requires also that Kq^2/η_M be smaller than Γ [12], which is satisfied only for the lowest end of the sampled q range, $q \lesssim 0.1$ nm^{-1}. The apparent success of the simplified theory over the extended q range (Fig. 1), therefore, is somewhat surprising. We note that the stacks of RHS are densely packed. The thickness of a DMPC bilayer at 30°C is 4.5 nm [25], implying that the solvent layers in-between membranes are only 1 nm thick. For such density and high-q surface perturbations the stack might not follow the usual description of linear smectic elasticity but respond merely as an anisotropic viscous liquid with surface tension.

In summary, the relaxation of nanoscale fluctuations in finite membrane stacks seems to occur via two distinct overdamped modes — a bulk baroclinic mode and a slower surface mode. The dispersion relation of the surface mode provides access to the dynamic surface tension of the stack, which should be hard to measure otherwise. Supplementing such an experiment with measurements at larger wavelengths (e.g., using dynamic light scattering), yielding a value for Θ, may allow the accurate extraction of the dynamic surface tension.

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